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Electron microscopy characterization of hot-pressed Al substituted $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$

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Abstract Hot-pressing was used to prepare a dense (97% relative density) cubic Al substituted $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ material at temperatures lower than typically used for solid-state and/or liquid phase sintering. Electron microscopy analysis revealed equiaxed grains, grain boundaries, and triple junctions free of amorphous and second phases and no Al segregation at grain boundaries. These results suggest that Al_2O_3 and/or Al cannot act as a sintering aid by reducing grain boundary mobility. If Al_2O_3 acts as a sintering aid its main function is to enter the lattice as Al to increase the point defect concentration of the slowest moving species.

Introduction

There is interest in the garnet $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) with the cubic structure as a fast Li-ion conducting solid electrolyte for use in Li-air and Li-sulfur batteries because, of its stability with Li and high lattice conductivity ($\sim 5 \times 10^{-4}$ S/cm) at room temperature [1, 2]. To use in Li-Air and Li-S batteries cubic LLZO with a high relative density (>95%) is required. Most of the previous approaches to consolidate the cubic LLZO powders have involved conventional solid-state or liquid phase sintering and have yielded materials in general with relative densities less than 95% [1–9]. In addition, most of the cubic LLZO materials that have been investigated at present contain Al intentionally added [3, 5–7, 10] or

from contamination during processing [2–4, 8, 9]. It has been suggested that Al serves two purposes: (1) stabilize the cubic structure [2–4, 7, 10] and/or (2) act as a sintering aid to increase final density [5, 7–9]. The role that Al plays in the stabilization of the cubic phase is not well-defined. Geiger et al. [4] has suggested that Al substitutes for Li and that this substitution may act to stabilize the cubic phase relative to the tetragonal phase. Geiger et al. [4] has postulated that an Al substitution on a Li site will lead to a reduction in Li content and increased Li vacancy concentration, both of which could affect phase stability and conductivity. However, a detailed mechanism was not proposed. For the case of solid-state sintering there is very little information about the location and distribution of Al intentionally added or from contamination in the microstructure of cubic LLZO and the mechanism of how Al aids densification is not known.

Hence, it is purpose of this note to examine the microstructure using electron microscopy of dense (relative density >95%) cubic LLZO prepared with intentionally added Al hot-pressed at temperatures below (1,000 °C), where any liquid phases can form to determine the location of the added Al to identify its role in densification.

Experimental

Single-phase cubic $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ powder was prepared by a solid-state method from Lithium Carbonate, Lanthanum (III) Hydroxide, Zirconium Oxide, and Aluminum Oxide precursors. It should be noted without the Al addition only a tetragonal phase was observed at room temperature after calcining. The Al composition (0.24 mol) chosen was based on the Al phase stability results [8]. The powders after mixing powders were calcined at 1,000 °C for 4 h. A boron nitride (BN) coating was used to prevent the

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Al_2O_3 crucible from reacting with the pellets. Previous results [8] using inductively coupled plasma (ICP) had shown that the BN coating prevented unwanted reactions with the Al_2O_3 crucible used for calcining the powders. Hot-pressing was chosen as the consolidation method, since this technique can lead to a high relative density at lower temperatures compared to conventional sintering [11]. The hot-pressing temperature of 1,000 °C was chosen based on the results of Jin et al. [7] to be below the temperature at which any liquid phase forms. After hot-pressing the resulting pellet was removed from the hot press and heated in air at 1,000 °C for 4 h to burn off residual graphite from the hot-pressing die. The hot-pressed disc was cut into rectangular parallelepipeds for microstructural analysis.

The microstructure of the hot-pressed sample was examined on fracture and polished surfaces using scanning electron microscopy (SEM). Thin-foil transmission electron microscopy (TEM) specimens were prepared from the rectangular parallelepipeds using conventional mechanical and ion milling techniques to produce an electron transparent region using a series of diamond lapping films and a precision ion polishing system (Fischione Ion Mill model 1010) at low temperature (−60 °C) with a finishing accelerating voltage of 0.5 kV. The microstructure of thin-foil specimens were examined using a Scanning Transmission Electron microscope (STEM) (JEOL 2100F field-emission microscope and an Oxford EDS (Energy Dispersive Spectroscopy) system) operated at 200 kV. Micro-analysis was undertaken using the EDS system in the STEM mode.

Results and discussion

X-ray diffraction confirmed that after hot-pressing and heat-treatment the pellet was single-phase cubic LLZO. No diffraction peaks corresponding to Al_2O_3 or LaAlO_3 were observed. The cation composition was measured by ICP analysis and the oxygen concentration was estimated to maintain charge neutrality. The exact composition of the material was $\text{Li}_{6.24}\text{La}_3\text{Zr}_2\text{Al}_{0.24}\text{O}_{11.98}$ (Al ~0.77wt%).

An SEM micrograph of the hot-pressed sample's fracture surface is shown in Fig. 1. From Fig. 1 several important points are noted. First, the material is very dense in agreement with the relative density ~97%, determined from the physical dimensions, weight, and the theoretical density of cubic $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$. Second, most of the voids are intergranular, there are very few intragranular voids. Third, a large portion of the fracture mode is mainly transgranular, indicating high grain boundary strength. Fourth, the grains are fairly equiaxed with an average linear intercept grain size ~3 μm . No second phases were observed. The SEM–EDS spectrum confirmed the presence

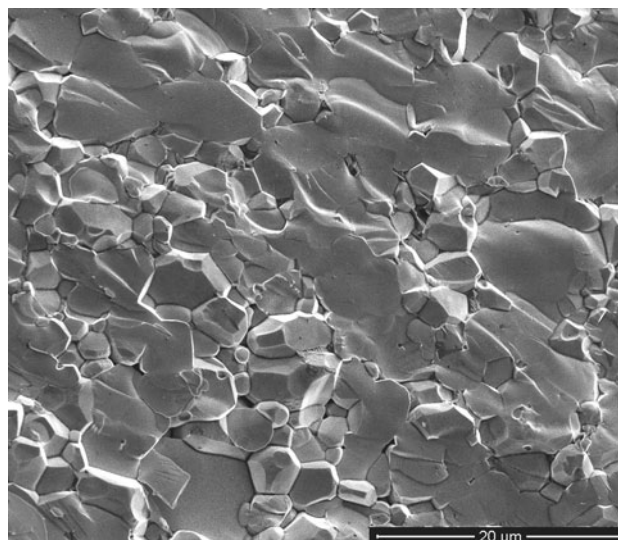


Fig. 1 SEM micrograph of a fracture surface from the hot-pressed $\text{Li}_{6.24}\text{La}_3\text{Zr}_2\text{Al}_{0.24}\text{O}_{11.98}$ material

of Al in the sample and suggested that it was uniformly distributed.

The LLZO grain boundaries and triple junctions were free of amorphous and second phases. No Al_2O_3 or LaAlO_3 phase particles were detected at grain boundaries and/or triple junctions. Figure 2 is a typical high resolution image of a clean grain boundary in the LLZO material. Figure 3 is typical example of a triple junction observed in the LLZO material. These results suggest the following: (1) the lack of any amorphous phase(s) at grain boundaries and triple junctions implies that during hot-pressing at 1,000 °C that no liquid phase(s) is present to assist densification, (2) the lack of oxide particles (i.e., Al_2O_3) at grain boundaries implies that they are not acting as sintering aids, by reducing grain boundary mobility [11], and (3) a majority of the added Al_2O_3 is in the form of Al, most likely in the

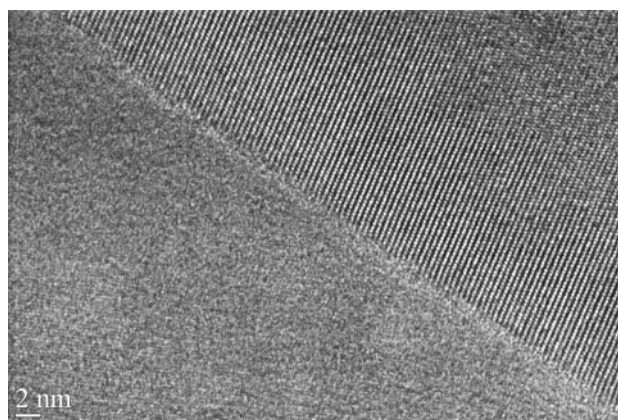


Fig. 2 HREM micrograph of a typical grain boundary in the hot-pressed $\text{Li}_{6.24}\text{La}_3\text{Zr}_2\text{Al}_{0.24}\text{O}_{11.98}$ material

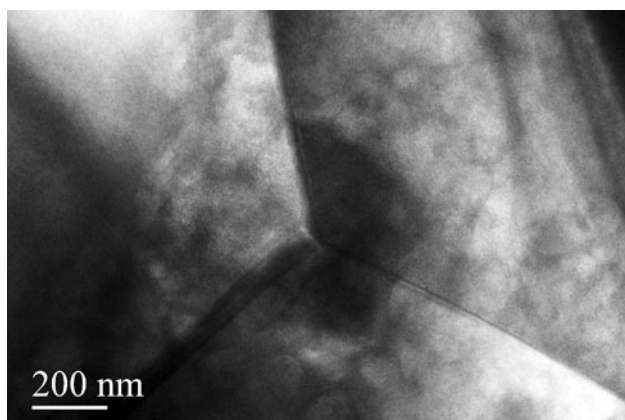


Fig. 3 Bright field TEM micrograph of a typical triple junction in the hot-pressed $\text{Li}_{6.24}\text{La}_3\text{Zr}_2\text{Al}_{0.24}\text{O}_{11.98}$ material

lattice. To confirm this suggestion TEM–EDS analysis for Al was conducted.

TEM–EDS analysis of grain interiors revealed the presence of Al in all grains analyzed (~ 10 grains). The Al concentration in the grains was determined using the Cliff–Lorimer ratio technique [12]. A theoretical value of the Cliff–Lorimer factor was used in the calculations. EDS analysis from locations within grain interiors yielded an Al concentration between ~ 0.2 and 0.3 mol. This value is in very good agreement with the amount measured by ICP (0.24 mol). This would suggest in a first approximation that a majority of the added Al_2O_3 in this experiment is entering the lattice LLZO lattice as Al. This result is in agreement with the suggestions of Geiger et al. [4] for LLZO of similar Al content (~ 0.19 mol) who postulated that during heating at high temperatures that Al from crucible (Al_2O_3) contamination entered the lattice on Li sites to replace Li lost as a result of heating at high temperature and the very recent TEM–EDS results Buschmann et al. [10] for cubic LLZO stabilized with the Al (~ 0.22 mol) who observed a homogenous distribution of Al.

The lack of any Al_2O_3 particles at grain boundaries suggests that the Al_2O_3 particles cannot be acting as sintering aids, by reducing grain boundary mobility. However, it is possible that Al itself is segregated at grain boundaries and can act as a sintering aid by reducing grain boundary mobility [10]. In order to check on this possibility, Al concentration profiles across grain boundaries were measured. Figure 4 shows a typical Al concentration profile across a LLZO grain boundary. Figure 4a is the bright field image showing the position of the analysis (bright spots) and Fig. 4b is the corresponding Al concentration (the zero position corresponds to the grain boundary). From Fig. 4 it can be seen that the Al concentration is roughly constant from the grain interior across the grain boundary to another grain interior; suggesting there is no Al segregation at grain boundaries. Al concentration profiles across other grain

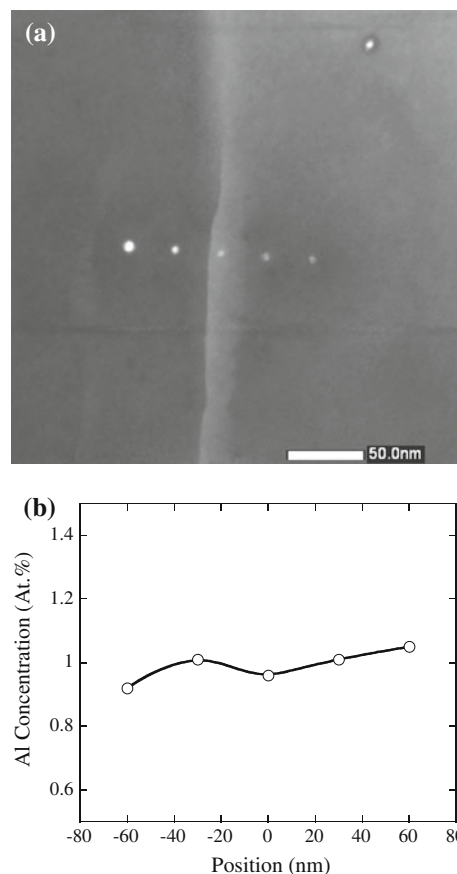


Fig. 4 **a.** Bright field TEM micrograph of a grain boundary in the hot-pressed $\text{Li}_{6.24}\text{La}_3\text{Zr}_2\text{Al}_{0.24}\text{O}_{11.98}$ material (bright spots are the positions where EDS analysis was conducted). **b.** Al concentration across the grain boundary shown in Fig. 4a. The zero position is the spot in the boundary

boundaries (~ 8) gave similar results, in that no Al segregation occurred at grain boundaries. In addition, Al line traces across several grain boundaries also suggested that there was no Al segregation at grain boundaries. Thus, at the Al concentration used in this experiment Al cannot act as a sintering agent by reducing grain boundary mobility [10].

The TEM observations reveal that for the added Al_2O_3 concentration used in the current experiments that a majority of it is entering the LLZO lattice as Al. It is uniformly distributed within the material. Based on these TEM observations it can be concluded: (1) Al enters the lattice; which most likely helps to stabilize the cubic structure compared to the tetragonal structure. This suggestion is in agreement with results of Shimonishi et al. [1], Kumazaki et al. [5], Jin et al. [7], and Rangasamy et al. [8] who found that with no Al, only the tetragonal structure was stable at room temperature. However, when a small amount of Al was added the cubic structure was stabilized at room temperature. (2) Al cannot aid sintering by reducing grain boundary mobility, and (3) if Al does aid

sintering to enhance densification, it is most likely by increasing the diffusivity of the species (slowest) that controls sintering. When Al enters the lattice as a result of charge neutrality this leads to an increase in the number of lithium vacancies [4, 8]. This increase in lithium vacancy concentration through point defect equilibrium reactions can lead to an increase in the concentration (i.e., hence, diffusivity) of the point defect of the species which controls sintering and thus, increasing final density.

Conclusions

Hot-pressing of cubic LLZO powders (Al $\sim 0.77\text{wt}\%$) lead to a highly dense material (relative density $\sim 97\%$) at temperatures below which a liquid phase forms. SEM and TEM analysis revealed an equiaxed grain morphology with a linear intercept grain size $\sim 3\text{ }\mu\text{m}$, grain boundaries, and triple junctions free of amorphous and second phases (i.e., Al_2O_3). TEM–EDS analysis revealed that there was no Al segregation to grain boundaries. The Al concentration within grains and near grain boundaries was in agreement with that measured by ICP. These results suggest the following for the Al concentration used in the present study: (1) that all of the added Al_2O_3 was entering the lattice as Al, (2) Al_2O_3 and/or Al cannot act as sintering aid by pinning down grain boundaries to reduce their mobility. If Al acts as a sintering aid its main function is to enter the lattice as Al to increase the concentration of the point defect of the species which controls sintering.

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